



## Room temperature imidazolium-based ionic liquids as scavengers for hydrogen sulfide removal of crude oil

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### ABSTRACT

Determination of H<sub>2</sub>S amounts in crude oil was performed by a precise method instead of UOP163 that were developed in our pervious works. Evaluation of ILs and scavengers were done by two ways. The first one was based on variable concentration of ILs as the scavenger (dynamic method), and the second one was based on a constant concentration of the scavenger during H<sub>2</sub>S removal process (static method). In the static method, design of experiments was performed for all three tested ILs and three parameters such as time, temperature, and dosage (injection volume) of ILs were investigated. A wide range of time and temperature was also studied according to operating conditions in petroleum terminals. The dose of ILs was obtained from the dynamic method. According to the obtained results, these ILs had a significant effect on H<sub>2</sub>S reduction in crude oil, so that H<sub>2</sub>S concentration in some conditions was less than 1 ppm. In comparison between ILs and commercial scavengers's performance can be properly understood that not only ILs reduced H<sub>2</sub>S concentration, but also their dosage was very low, and mole ratio of [IL]/[H<sub>2</sub>S] was 1:3 that it was negligible compared with commercial scavengers. Also the results showed that [EMIM][NTf<sub>2</sub>] was more effective than the other ILs in H<sub>2</sub>S removal.

### Keywords:

H<sub>2</sub>S removal

Crude oil

Ionic liquids

Commercial scavengers

Petroleum refining

### 1. Introduction

Hydrogen sulfide is one of the most abundant sulfur containing compounds in natural gas and light and middle distillate oil fractions as well as in atmospheric air effluents and pulp and paper industry. Hydrogen sulfide is undesirable, colorless, odorous, highly toxic, and poisonous for catalysts and corrosive to industrial gas and oil streams [1-3]. Also, it can be regarded as a major source of air pollution [4-6]. This acid gas is produced

along with methane and light hydrocarbons in many oil and gas fields [7, 8]. According to the international environmental regulations, H<sub>2</sub>S contained in the acid gases should be effectively removed before emission to atmosphere [8, 9]. H<sub>2</sub>S is commonly removed from natural and synthesis gases through chemical absorption using aqueous solutions of organic bases like single amines, amine mixtures, or mixtures of an amine and a salt of an amino acid [10-12]. Extensive research has been conducted by several groups on aqueous solutions of alkanolamines, especially

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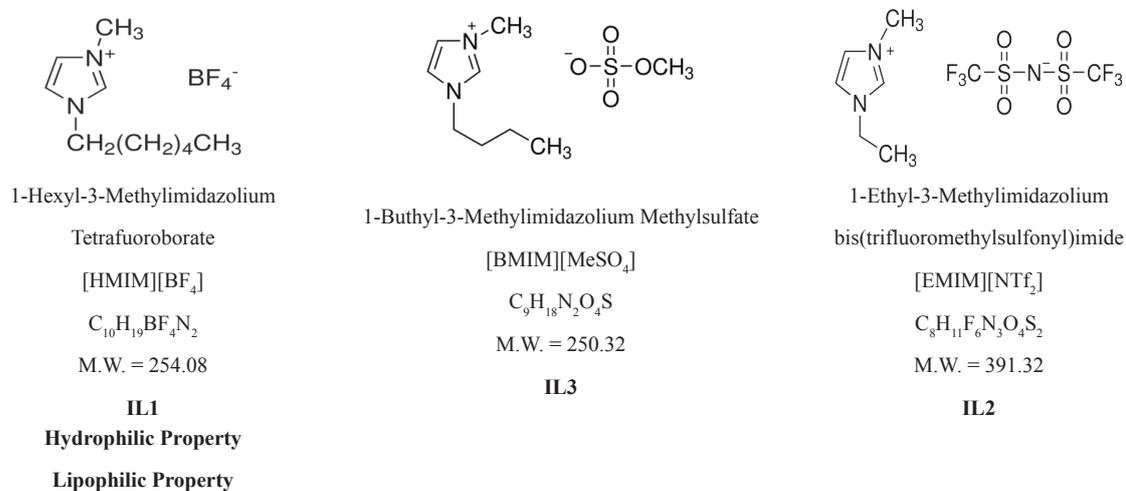
monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) for treating and sweetening [13-16]. All of them are volatile and they show a reversible reaction that it can reverse  $H_2S$  in refining processes and make the process economically expensive [17].

In contrast ionic liquids (ILs) provides a vaporless, thermally stable [18, 19], reusable “green” solvent and catalyst for chemical reactions, so ILs has very possibility for removal of  $H_2S$ . ILs are molten salts composed entirely of ions, and many of them are liquids at room temperature. Room temperature ionic liquids (RTILs), often referred to as ‘designer solvents’, have been the great focus of scientists in various fields since they can be tuned for specific applications [20-27]. Nowadays, the most commonly studied ILs normally contain, imidazolium, ammonium, phosphonium, pyridinium, and pyrrolidinium cations, and tetrafluoroborate, hexafluorophosphate, bistrifluorosulfonylimide and triflate anions [20, 25, 28-30]. In addition, the physicochemical properties of ILs can be finely tuned by slight structural changes of the corresponding cations and anions [23–26]. To better understand the nature of ionic liquids and rationally expand their applications especially as pollutant scavenger and electrolyte, knowledge of their thermophysical

and electrochemical properties is required. In this work [Hmim][BF<sub>4</sub>], [Emim][Ntf<sub>2</sub>] and [Bmim][MeSO<sub>4</sub>] were used as scavengers for  $H_2S$  removal from crude oil and then the results were compared with several commercial scavengers. Molecular structures of the three ILs are shown in Fig. 1.

In our previous work, physical and electrochemical properties of these ILs were investigated. Viscosity, solubility, thermal decomposition and electrochemical window of three ILs were studied more than the other properties. So these mentioned properties have been applied for  $H_2S$  removal. For example, the viscosity of selected ILs was fully compatible with the crude oil. Therefore, use of them in crude oil was not a problem. The thermal stability of ILs was very high and their ability at high temperatures was excellent. ILs may have hydrophilic or lipophilic properties.

The hydrophilic and lipophilic ILs can remove  $H_2S$  of aqueous and organic parts of crude oil respectively. The decomposition temperature ranges of three ILs are shown in Table 1. Also, the experimental values of physicochemical properties of [HMIM][BF<sub>4</sub>], [EMIM][NTf<sub>2</sub>] and [BMIM][MeSO<sub>4</sub>], such as density, refractive index, dynamic and kinematic viscosities, pH, and surface tension are listed in Table 2[20]. According to our previous studies these ILs are very suitable for  $H_2S$



**Fig. 1.** Molecular structures of the three ILs

scavenging and to the best of our knowledge we didn't find any paper related to H<sub>2</sub>S removal from crude oil by using ILs. In addition, these ILs unlike other scavengers don't have any disadvantages such as slow synthetics, high consumption, unstable in high temperatures, or increase salt and sediments content. Of course the elimination

**Table 1.** Thermal decomposition for investigated ionic liquids.

Ionic Liquid	Decomposition Temperature Range/°C
[HMIM][BF <sub>4</sub> ]	310-500
[EMIM][NTf <sub>2</sub> ]	390-510
[BMIM][MeSO <sub>4</sub> ]	317-438

**Table 2.** Density  $\rho$ , dynamic viscosity  $\eta$ , refractive index  $n_D$ , surface tension  $\sigma$ , thermal expansion  $a_p$ , and pH of the ionic liquids at different temperatures

t (°C)	$\rho$ (g mL <sup>-1</sup> )	$\eta$ (mPa s)	$n_D$	$\sigma$ (mN m <sup>-1</sup> )	$10^4 a_p$ (K)	pH of 1% Solution
<b>[HMIM][BF<sub>4</sub>]</b>						
10	1.1562	608.1	1.4265	41.4	5.343	
20	1.1492	311.7	1.4241	40.6	5.525	6.41
25	1.1461	220.0	1.4223	40.4	5.623	6.25
30	1.1425	167.3	1.4211	40.0	5.718	
40	1.1355	103.3	1.4183	39.8	5.909	5.77
50	1.1280	63.77	1.4158	39.0	6.104	
60	1.1214	52.22	1.4137	38.2	6.302	5.12
70	1.1122	28.48	1.4106	37.2	6.504	
80	1.1004	21.39	1.4080	36.6	6.709	4.49
90	1.0874	15.87	1.4051	36.3	6.918	4.17
95	1.0838	13.92	1.4038	35.9	7.025	
<b>[EMIM][NTf<sub>2</sub>]</b>						
10	1.5311	55.92	1.4254	40.2	4.706	
20	1.5220	37.27	1.4232	39.8	5.518	6.48
25	1.5168	31.13	1.4220	39.4	5.929	6.5
30	1.5117	26.28	1.4206	39.0	6.344	
40	1.5020	19.67	1.4179	38.8	7.186	6.54
50	1.4907	14.96	1.4153	38.6	8.045	
60	1.4780	11.84	1.4127	38.0	8.925	6.60
70	1.4651	9.506	1.4101	37.2	9.828	
80	1.4494	7.820	1.4072	36.6	10.76	6.66
90	1.4292	6.539	1.4045	36.0	11.72	6.69
95	1.4230	6.054	1.4033	35.5	12.21	
<b>[BMIM][MeSO<sub>4</sub>]</b>						
10	1.2117	220.6	1.4831	46.0	4.457	
20	1.2053	122.3	1.4777	44.4	4.810	7.60
25	1.2019	93.78	1.4771	43.7	4.988	7.55
30	1.1983	73.35	1.4765	43.4	5.167	
40	1.1923	46.85	1.4745	42.6	5.530	7.39
50	1.1853	32.21	1.4719	42.0	5.899	
60	1.1774	23.02	1.4694	41.2	6.274	7.18
70	1.1668	17.05	1.4673	39.8	6.656	
80	1.1538	13.14	1.4650	39.0	7.0453	6.96
90	1.1400	10.34	1.4626	38.1	7.443	6.85
95	1.1356	9.257	1.4615	37.6	7.645	

reaction mechanism is unknown and our further studies certainly will be in this field.

In present work determination of  $H_2S$  amounts in crude oil was performed by the method that was presented by researchers at Research Institute of Petroleum Industry method (RIPI). [31] Then ILs was used in two different ways as scavengers for  $H_2S$  removal. Finally, the results of both methods were compared with several commercial scavengers. Also, in our next work, metallic nanoparticles will be synthesized in ionic liquids media for  $H_2S$  removal from crude oil.

## 2. Experimental

### 2.1. Materials

All chemicals and three ionic liquids were purchased from Merck, Aldrich and Fluka companies. The chemicals were used without further purification. Crude oil samples included exported crude oil such as Balarood, Masjed Soleyman, Soomar, Bahregan, and Furoozan.

### 2.2. Experimental procedure

The RIPI method was applied for determination of  $H_2S$  amounts in crude oil. As we have previously reported this method was based on preliminary extraction with voltammetric detection. This method offers several inherent advantages for  $H_2S$  determination. Voltammetric detection methods are specific, since other species are electrochemically inactive at potentials where  $H_2S$  is detected. Also, this technique is very sensitive. Apparatus for determination of hydrogen sulfide in crude oil is shown in figure 2. After the measurement of  $H_2S$  content in crude oil, evaluation of several commercial scavengers and the ILs was done. Unfortunately there was not a systematic and standardized method to evaluate the efficiency of scavengers. In present work two methods was applied for evaluation. One is related to RIPI, was based on constant concentration of ILs or commercial scavengers and the other one was based on variable concentration of them that is related to

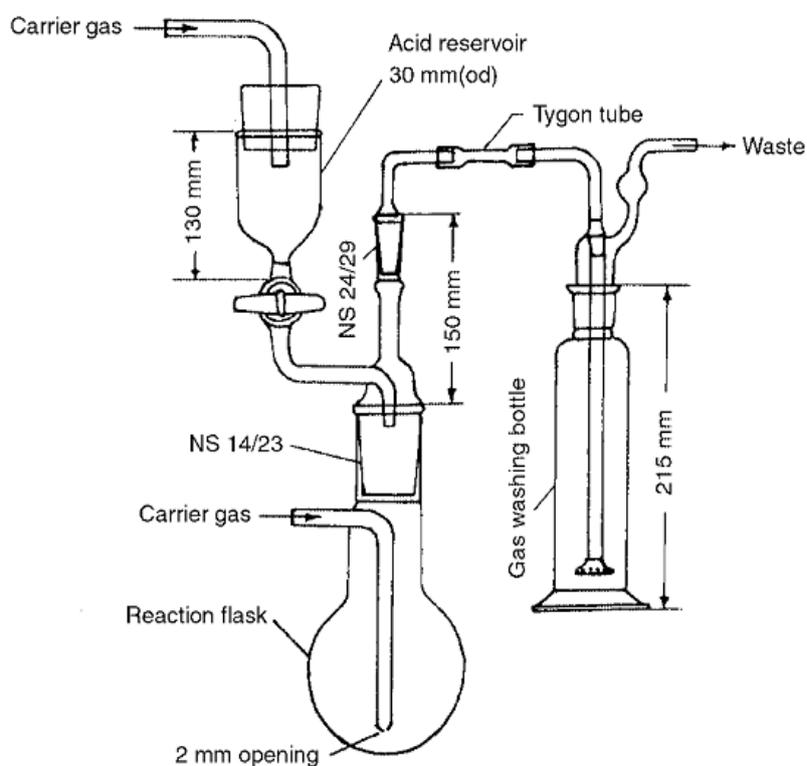


Fig. 2. The apparatus for determination of hydrogen sulfide in crude oil

oil export terminals. In the constant concentration method for ILs, design of experiment was applied by using Design Expert software.

### 3. Results and discussion

#### 3.1. Evaluation of commercial scavengers

Evaluation of commercial scavengers was developed by two methods.

##### 3.1.1 First method (Variable concentration)

This method has been developed by the RIPI, had high operating speed. The scavengers that were used had fast kinetic and high efficiency. Evaluation in this method was based on measuring and following potential variations of crude oil during addition of scavengers in a specified time. A potential variation of crude oil was shown in figure 3.

In the RIPI method, usually in the one minute intervals, approximately 50  $\mu\text{L}$  of scavenger was added to the certain amount of crude oil (about 100 g) and potential changes versus time and volume

consumption of scavenger were recorded (Fig.3). Mutations that occurred in the potential curves were related to the equivalent point of  $\text{H}_2\text{S}$  titration by scavenger. In the equivalent point, almost all  $\text{H}_2\text{S}$  contents were neutralized by scavenger and crude oil are free of  $\text{H}_2\text{S}$ .

Primary investigations showed that electrode potential was depended on  $\text{H}_2\text{S}$  or S concentration in crude oil. As long as hydrogen sulfide was present in the crude oil, electrode potential, depending on the  $\text{H}_2\text{S}$  concentration in the specified range was nearly between -900 up to -1200 mV. It should be noted that beside  $\text{H}_2\text{S}$  concentration the electrode potential could be a function of temperature and electrolyte. Also, according to the Nernst equation, the electrode potential is depend on oxidative and reductive concentration, ions mobility and activity coefficient. Therefore, the potential ranges difference between -900 to -1200 mV may be due to one of the items listed above. In this method, evaluation of  $\text{H}_2\text{S}$  reduction was based on

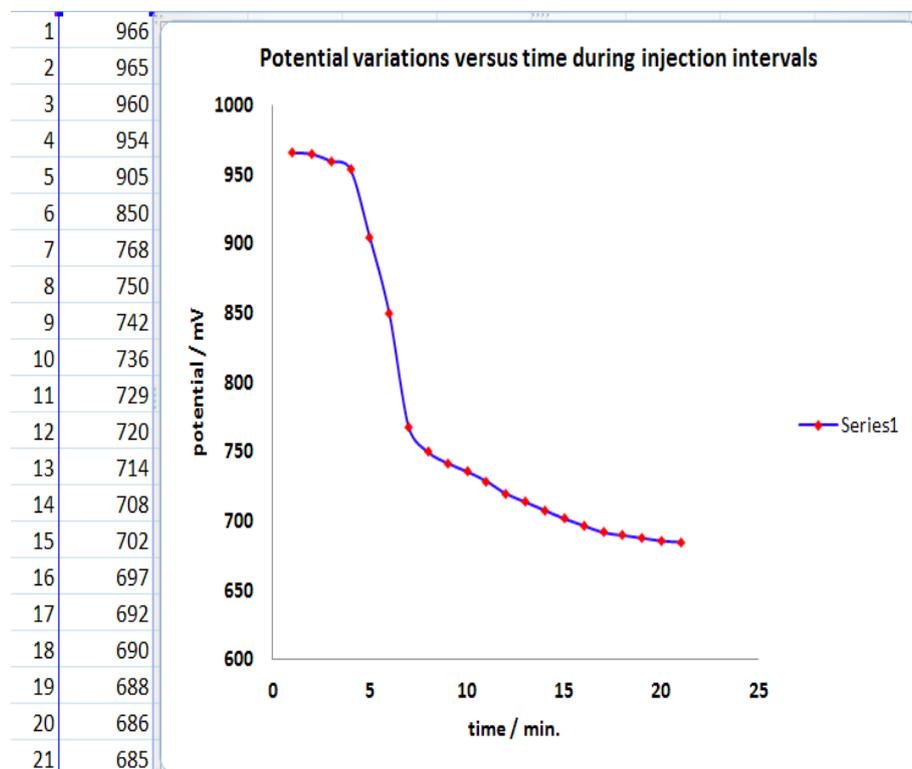


Fig. 3. Potential variations of crude oil by addition of a commercial scavenger versus time.

**Table 3.** Evaluation of commercial scavengers using RIPI method

Sample name	Injection volume/ml	E (initial)/mv	E (final)/mv	Treatment time/min
sulfavent 32	0.65	1100	805	15
sulfavent 42	0.55	1080	810	10
sulfavent 43	1	1000	860	7
sulfavent 44	1	1100	945	12

decreasing of the electrode potential. Experience indicated that when the crude oil was free of  $H_2S$ , electrode potential shifted to nearly less than -750 up to -800 mV. To more accurate investigations, 4 samples of commercial scavengers were tested using this method, and the results are given in Table 3.

As can be observed, sulfavent 32 and sulfavent 43 had better efficiency than the others. Lesser amounts of sulfavent 32 were used, on the other hand, Sulfavent 43 had higher speed. So that, for the neutralization of  $H_2S$  in crude oil, only 1 ml of scavenger was needed during 7 minutes. Although, both methods gave same results in the selection of scavengers, but the RIPI method provided more information, such as the effective time of scavenger and equivalent point.

### 3.1.2. Second method (Constant concentration)

This method was based on instructions of oil export terminals. First, the amount of  $H_2S$  was measured in crude oil and then specific dosage of scavengers was added to the crude oil. The consumed volume of scavenger (was related to  $H_2S$  concentration. Here,  $H_2S$  concentration was based on the

amount of hydrogen sulfide in crude oil, which is usually between 50 to 100 ppm of scavenger and depending on its efficiency, was about 2 to 5 times of the amount of  $H_2S$  in crude oil.

In a general evaluation, 100 g of a crude oil containing 75 ppm  $H_2S$ , was chosen. Then 225 ppm ( $[Scavenger]/[H_2S]:3$ ) of the scavenger was added to it. After an hour stirring at room temperature, the  $H_2S$  concentration was measured with RIPI method. The same experimental conditions were done for an overnight and the results were reported and compared. Accordingly, all four samples were tested and the results are shown in Table 4.

Since the experiments were conducted on consecutive days, and there was no possibility of  $H_2S$  amount stabilization. So, the results were normalized in first and the last columns. As can be seen in the table, without any commercial scavenger,  $H_2S$  concentration has reached to 43 ppm after an overnight, but by mistake this reduction was generally considered to be scavenger. As a result, long reaction time was one of disadvantages in this method.

The result showed that all scavengers, with the exception of Sulfavent 44, had the ability to remove

**Table 4.** Evaluation of commercial scavengers using constant concentration of scavenger

sample name	$H_2S$ content in crude befor treatment / ppm	$H_2S$ content in crude after 1 hour treatment / ppm	$H_2S$ content in crude after overnight treatment / ppm	$H_2S$ content in crude before treatment after overnight / ppm
sulfavent 32	75	10.5	< 1.0	43
sulfavent 42	75	47.0	< 1.0	43
sulfavent 43	75	5.4	< 1.0	43
sulfavent 44	75	26.0	< 17	43

H<sub>2</sub>S from crude oil. Whereas both Sulfavent 32 and 43 had satisfactory results after an hour. It seems that this method, where to store crude oil before loading, is appropriate. In the second method, which was developed by RIPI, those of scavengers that had rapid reaction kinetics (less than 15 min) will be successful in reduction or elimination of H<sub>2</sub>S from crude oil.

### 3.2. Evaluation of Ionic Liquids

#### 3.2.1 First method (Variable concentration)

The basis of this method, as was explained in the case of scavengers, was based on gradual addition of ionic liquids and measuring and following potential variations of crude oil. First, the amount of H<sub>2</sub>S was measured in crude oil, then 20 ml of isopropyl alcohol and 30 ml of toluene was added to 50 g of crude oil that containing 100 ppm of H<sub>2</sub>S. At the beginning, electrode potential was read, then certain amount of ionic liquid (approximately 10  $\mu$ l) was added to crude oil in the same time intervals and potential variations was recorded. Fig. 4 shows the potential variations versus time for three ionic liquids. Also, in this method, the required volume

of ionic liquid to minimize concentration to less than 15 ppm of H<sub>2</sub>S was determined. When the electrode potential shifted to less than -800 mV, H<sub>2</sub>S concentration was less than 15 ppm.

As can be seen in this chart, the ILs have been able to reduce H<sub>2</sub>S concentration to less than 1 ppm, in a short time (less than 30 minutes). Also, the mole ratio of [IL]/ [H<sub>2</sub>S] was 2.3, 1.3, and 2.5 for [HMIM][BF<sub>4</sub>], [EMIM][NTf<sub>2</sub>], and [BMIM][MeSO<sub>4</sub>] respectively that these were equal to 75  $\mu$ l, 48  $\mu$ l and 76  $\mu$ l of ionic liquids. These values were negligible in comparison to commercial scavengers. Also among the three ionic liquids, [EMIM] [NTf<sub>2</sub>] had a higher efficiency in H<sub>2</sub>S removal from crude oil. Since [EMIM] [NTf<sub>2</sub>] is lipophilic and its viscosity is closer to crude oil's viscosity, it can be better H<sub>2</sub>S scavenger, moreover the consumed volume of IL<sub>2</sub> is less than the others.

#### 3.2.2. Second method (Constant concentration)

In this method, the H<sub>2</sub>S concentration was measured in 15 g of crude oil, then specific dosage or concentration of ionic liquid was added to the crude oil. In fact, according to the dynamic

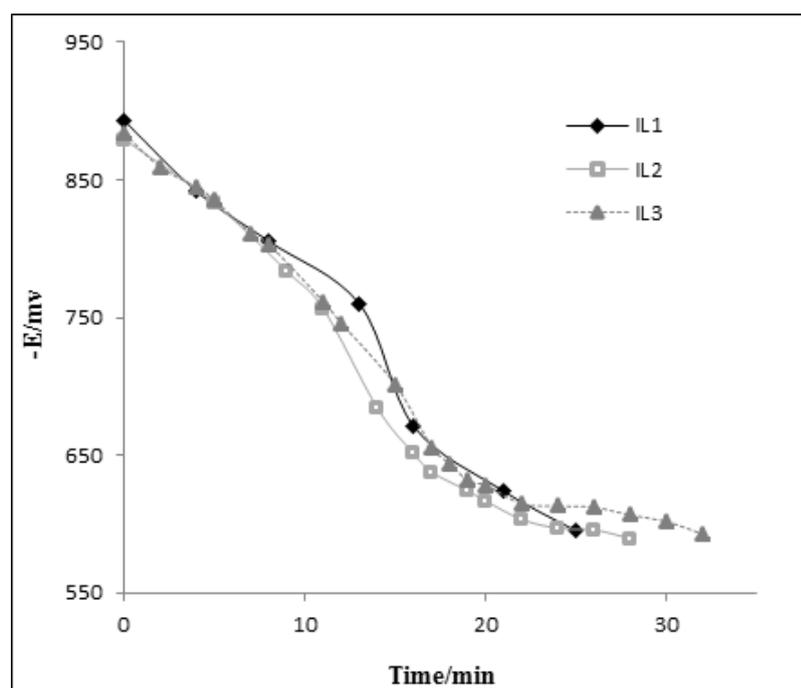


Fig. 4. The electrode response versus time during the gradual addition of the ionic liquid in crude oil.

method results and operating condition in crude oil terminals, the required time, temperature and dosage of ILs, were determined for H<sub>2</sub>S removal. Finally, after considering the conditions in crude oil terminals (crude oil temperature, scavenger dosage and duration the crude oil passes through pipeline) and according to dynamic method results, it can be concluded that the required amount of ILs to remove H<sub>2</sub>S should be selected from 1 to 3 [IL]/[H<sub>2</sub>S] mole ratio, the reaction time from 25 min to 35 min and the temperature from 20° C to 50° C, should be selected. After identifying these factors design of experiment was performed for each IL, using Design Expert software.

### 3.2.3. Design of experiment

As mentioned, the effective parameters or factors on H<sub>2</sub>S concentration was detected by using dynamic method. Then design of experiment was performed using Expert design software that

contained 20 runs or tests for each IL and various conditions such as dosage, temperature and reaction time, was applied separately for each run. The results are given in Table 5. As can be seen in this table, first the concentration of H<sub>2</sub>S was 100 ppm and after applying various conditions, such as dosage, time and temperature, H<sub>2</sub>S concentration was reduced even less than 1 ppm. Columns 5 to 8 were normalized, because in some cases, H<sub>2</sub>S concentration was more than 100 ppm, therefore all results were normalized to 100 ppm. It is obvious that if IL dosage, time and temperature was grater, H<sub>2</sub>S concentration was lower.

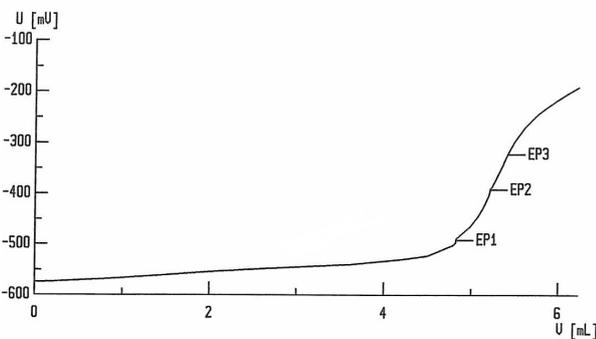
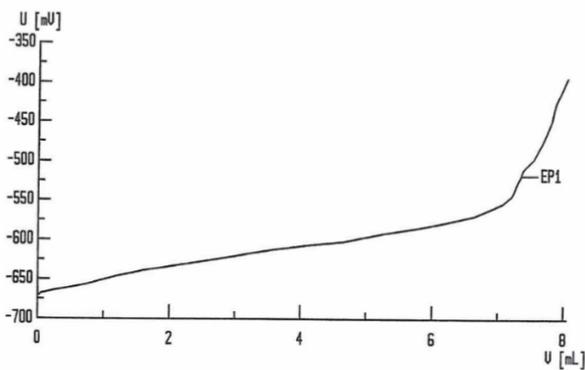
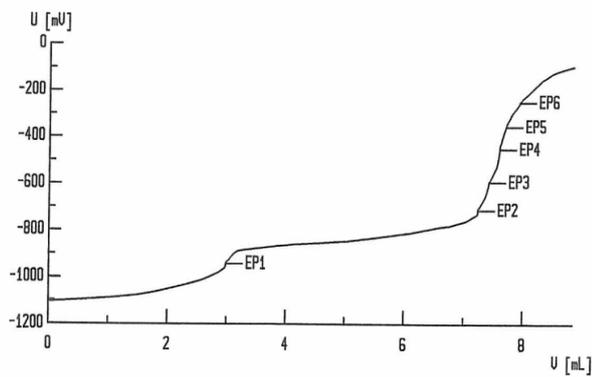
Runs 4 and 14 for IL2 and crude oil sample without using ionic liquids are briefly reviewed in Table 6. H<sub>2</sub>S concentration at the beginning was 113.27 ppm that was normalized to 100 ppm after 35 min stirring at 30 °C. The electrode potential shifted to -675 mV indicated that H<sub>2</sub>S concentration was reached to less than 1 ppm. Also after run 14, H<sub>2</sub>S

**Table 5.** Design of experiment for three ionic liquids

Run Order	Temp/ °C	Time /min	Dose [IL]/[H <sub>2</sub> S]	ppm H <sub>2</sub> S before treatment	ppm H <sub>2</sub> S IL1	ppm H <sub>2</sub> S IL2	ppm H <sub>2</sub> S IL3
1	35	30	2	100	21.3	27.3	14.82
2	20	25	1	100	78.5	32.5	62.95
3	35	30	2	100	17.2	22.46	19.63
4	50	35	1	100	<1.0	<1	<1
5	20	35	3	100	<1.0	9.3	17.51
6	50	25	3	100	<1.0	4.02	<1
7	35	30	2	100	19.0	20.79	19.85
8	35	30	4	100	<1.0	7.3	3.1
9	35	30	0.4	100	38.5	48.9	27.46
10	11	30	2	100	32.3	41.83	26.27
11	35	30	2	100	18.4	18.55	19.04
12	60	30	2	100	<1.0	3.93	<1
13	35	22	2	100	21.4	30.47	35.79
14	35	38	2	100	<1.0	8.2	4.34
15	35	30	2	100	20.7	21.41	17.69
16	35	30	2	100	19.2	19.10	15.60
17	20	35	1	100	6.1	11.1	38.25
18	50	35	3	100	<1.0	<1	<1
19	50	25	1	100	8.4	11.3	<1
20	20	25	3	100	23.3	14.32	24.55

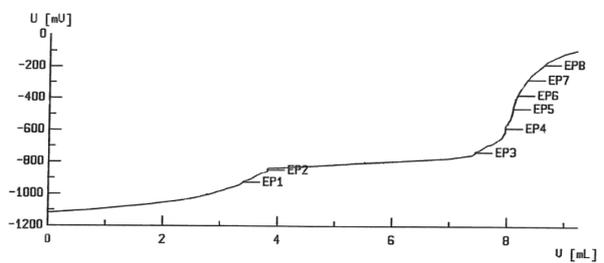
**Table 5.** Continue of Design of experiment for three ionic liquids.

	weight	Volume consumption of AgNO3	Initial potential (mV)	H <sub>2</sub> S (ppm)	Condition		
					Time (min)	Temperature (°C)	Dose [IL]/[H <sub>2</sub> S]
Crude oil	10.2	7.2	-1100	113.3	-	-	-
IL2 (Run 4)	15.0	-	-670	<1.0	35	50	<b>1</b>
IL2 (Run 5)	15.0	-	-575	<1.0	35	20	<b>3</b>

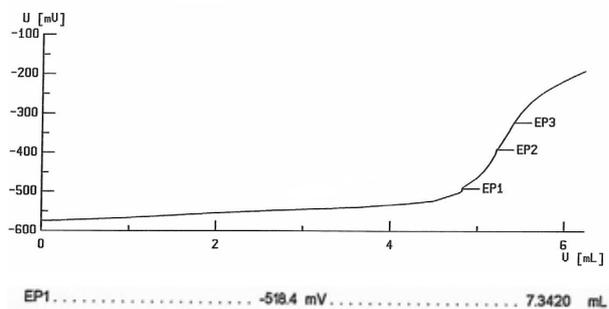
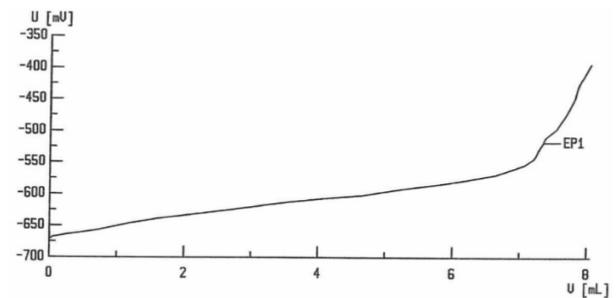


**Fig. 5.** The electrode potential versus volume of silver nitrate for H<sub>2</sub>S measurement in crude oil.

EP1	-926.9 mV	3.3854 mL
EP2	-850.7 mV	3.8148 mL
EP3	-735.7 mV	7.4372 mL
EP4	-585.0 mV	7.9573 mL
EP5	-461.4 mV	8.0862 mL
EP6	-376.5 mV	8.1608 mL
EP7	-279.3 mV	8.3390 mL
EP8	-184.0 mV	8.6172 mL



**Fig. 6(a).** The electrode potential versus volume of silver nitrate for H<sub>2</sub>S measurement in crude oil that contains IL2.



**Fig. 6(b).** The electrode potential versus volume of silver nitrate for H<sub>2</sub>S measurement in crude oil that contains IL2

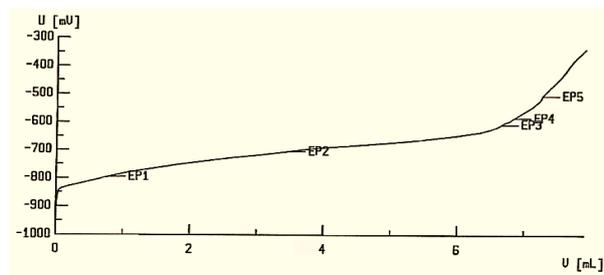
concentration was decreased from 113.27 ppm to less than 1 ppm. The potentiometric curves for crude oil, runs 4 and 14 are presented respectively in figure 5.

The first chart showed  $H_2S$  concentration before addition of ionic liquids and the second one showed  $H_2S$  concentration after addition of ionic liquids in a special time and temperature. The electrode potential versus volume of silver nitrate was shown in Fig.5 and  $H_2S$  concentration can be calculated before and after of ILs addition, according to the following formula.

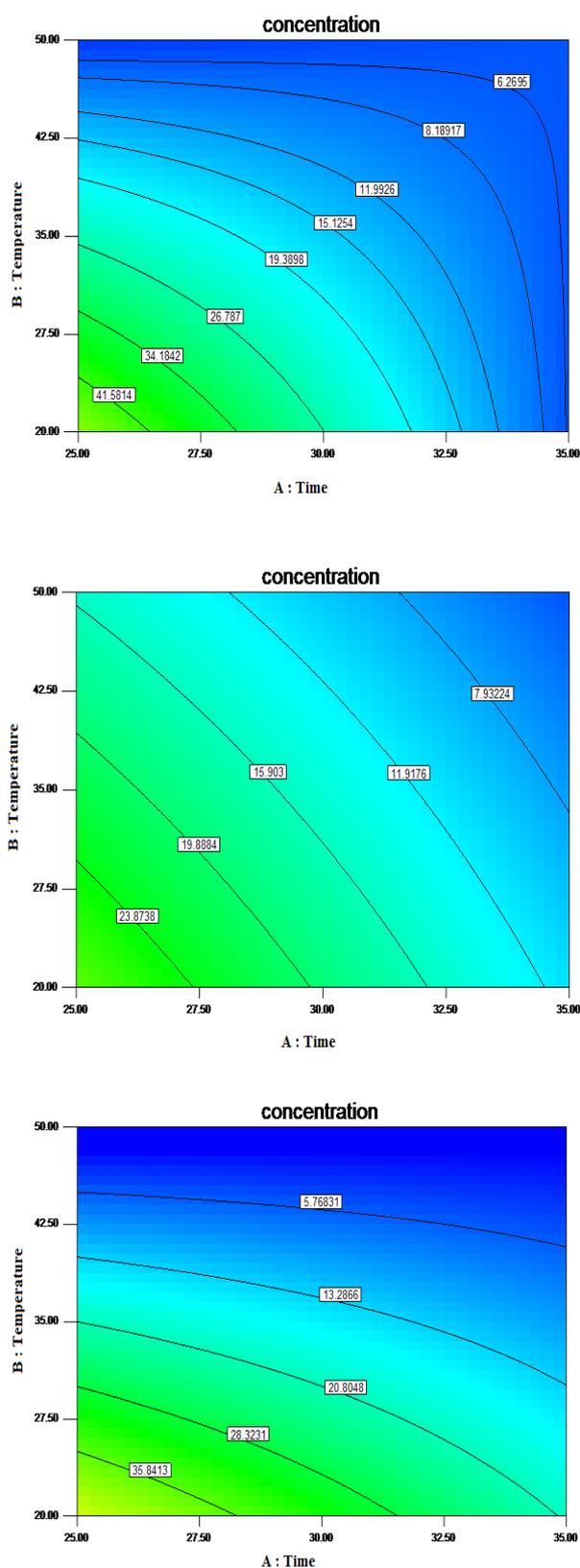
$H_2S$  concentration before Run 4 and Run 14 for [EMIM][NTf<sub>2</sub>] was 116.66 ppm as shown in figure 6a and 6b.  $H_2S$  concentration was diminished to less than 10 ppm after the Runs 4 and 14. figure 7 and 8 showed the electrode potential versus volume consumption of silver nitrate for runs 4 and 14 respectively. The EP3 (third equivalent point) for run 4 and EP1 for run 14 showed the required volume consumption of silver nitrate that neutralized  $H_2S$  amounts in crude oil.

Because the electrode potential was started with -675 mV, as a result  $H_2S$  concentrations is less than 1 ppm.

We found that all three parameters had significant effect in  $H_2S$  removal by obtained results of this software. Here a few charts are examined briefly in figure 8.



**Fig. 7.** The electrode potential versus volume of silver nitrate for  $H_2S$  measurement in crude oil that contains IL2.



**Fig. 8.** Curves of temperature versus time at constant dosage.

These figures showed that at constant dosage, if temperature and time were greater, H<sub>2</sub>S concentration was less. Also [EMIM][NTf<sub>2</sub>] had better efficiency than the other ILs in H<sub>2</sub>S removal, because it reduced H<sub>2</sub>S concentration to less than 15 ppm in a short time.

#### 4. Conclusions

The results showed that all three ionic liquids were chosen correctly, because all of them are suitable for H<sub>2</sub>S removal from crude oil. The investigation of chemical and physical properties of ionic liquids that all results were presented in our previous work, were indicated that some properties such as high thermal stability, pH, solubility, and wide electrochemical windows, defined them as a suitable scavenger to H<sub>2</sub>S removal. Using ionic liquids in the limited situation, and at low concentrations of H<sub>2</sub>S, is effective for crude oil sweetening. In comparison between commercial scavengers and ionic liquids and according to the obtained results from dynamic method and design of experiments, it is found by us that ILs is more effective than commercial scavengers because the volume consumption of ILs is less than the scavengers. Also, ILs could reduce H<sub>2</sub>S concentration to less than 1 ppm. In design of experiments, three parameters (dosage, time and temperature) were investigated which all of them are effective in H<sub>2</sub>S removal, and time is the most effective parameter. In addition, the results of dynamic method and design of experiment show that [EMIM][NTf<sub>2</sub>] has better performance; in addition, the lower dosage of it has been spent.

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